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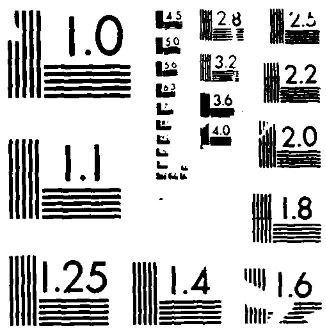

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A Remark on Radiative Decay Rates for Molecules Near a Dielectric Sphere

by

P. T. Leung, Young Sik Kim Thomas F. George

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Departments of Chemistry and Physics
State University of New York at Buffalo
Buffalo, New York 14260

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A REMARK ON RADIATIVE DECAY RATES FOR MOLECULES NEAR A DIELECTRIC SPHERE

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ABSTRACT

A model for radiative decay rates of molecules near a dielectric sphere by Gersten and Nitzan is analyzed and compared to the results from an exact dynamical theory.

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In a series of papers, we have carried out critical assessments of the validity of the static image theory (IT) as applied to the problem of the classical decay rates of molecules near a dielectric surface,[1-3] where the role of the dynamical energy transfer theory (ET) has been emphasized for the cases where the surface is flat,[1] spherical[2] and of shallow roughness.[3] In particular, we have shown that IT can be very inaccurate for highly-conducting substrates and that, strictly speaking, the radiative rates cannot be described within IT. However, it is interesting to note that in a series of paper, Gersten and Nitzan (GN) succeeded in incorporating the radiative rates into IT for a spheroidal substrate via a simple, approximate model.[4] It is the purpose of this communication to assess the accuracy of the GN model for the radiative rates, where we shall consider a dielectric sphere as the substrate throughout.

The total decay rate can be expressed as the sum of the radiative and nonradiative transfer rates,[4]

$$\gamma = \gamma^{R} + \gamma^{NR} \quad , \tag{1}$$

where

$$\gamma^{R} = \frac{1}{W} \int_{(r\to\infty)} d\Omega \; r^{2} \; \vec{S} \; \hat{n} \quad , \tag{2}$$

and

$$\gamma^{NR} = \frac{1}{2W} \int_{V} d\tau \; \sigma \; |\vec{E}|^{2} \quad , \tag{3}$$

where $\vec{S} = \frac{c}{8\pi} \mathrm{Re}(\vec{E}\times\vec{H}^*)$ is the Poynting vector, σ is the conductivity of the substrate, W is the average energy of the dipole, $d\Omega$ is the differential element of the solid angle, and $d\tau$ is the differential volume element. The integral in Eq. (2) is over a surface at infinity while that in Eq. (3) is over the volume of the dissipative substrate. For a dipole above a sphere of dielectric constant ϵ, the solutions for the exact dynamical fields and hence the decay rates have been reported in the literature,[2,5] where previous comparison with the static theory (IT) shows that as long as the distance (d) between the molecule and the spherical surface is much smaller than the emission wavelength (λ) and that the conductivity of the sphere is not too high, IT should give results for the fields very close to those from ET.[2] Hence, we expect that γ^{NR}, which is important only for close distances d, can be treated with reasonable accuracy in the non-retarded theory as in GN's approach.[4] However, it is not difficult to see that if one substitutes directly the fields from IT into Eq. (2), one gets γ^R 0 since $\lim_{r\to\infty} r^2\vec{S}\cdot\hat{n} = 0$ for fields from IT.[2] Thus it appears that a straightforward application of IT cannot incorporate the radiative transfer for the decay problem. Nevertheless, GN has considered the following model to calculate γ^R. By calculating the total induced dipole moment for the sphere from IT[4]

$$\vec{\mu}_{in} = \frac{1}{4\pi} \int_V d\tau \; (\epsilon - 1)\vec{E}_{IT} \quad , \tag{4}$$

the dipole-sphere system is then regarded as one free dipole system with total moment $\vec{\mu}_0 + \vec{\mu}_{in}$ oscillating with the same frequency as the original molecular dipole $\vec{\mu}_0$. Hence, because of this "single-system approximation", the possible interference between the fields in the radiation zone emitted by the two dipoles $\vec{\mu}_0$ and $\vec{\mu}_{in}$ (which are actually at different locations) cannot be included in this

approach. The radiative rates (normalized with respect to the free-molecule rate γ_0) thus obtained are then given by[6]

$$\frac{\gamma_\perp^R}{\gamma_0} = \left|1 + 2\left(\frac{a}{a+d}\right)^3 \frac{\epsilon-1}{\epsilon+2}\right|^2 , \tag{5}$$

$$\frac{\gamma_\parallel^R}{\gamma_0} = \left|1 - \left(\frac{a}{a+d}\right)^3 \frac{\epsilon-1}{\epsilon+2}\right|^2 , \tag{6}$$

where a is the radius of the sphere, and $\perp$ and $\parallel$ denote the radial and tangential orientation of the dipole, respectively. On the other hand, the results from the exact dynamical theory (ET) can be expressed as[2,5]

$$\frac{\gamma_\perp^R}{\gamma_0} = \frac{3}{2} \sum_{n=1}^{\infty} n(n+1)(2n+1) \left|\frac{j_n(y) + B_n h_n^{(1)}(y)}{y}\right|^2 , \tag{7}$$

$$\frac{\gamma_\parallel^R}{\gamma_0} = \frac{3}{4} \sum_{n=1}^{\infty} (2n+1)\left(\left|j_n(y) + A_n h_n^{(1)}(y)\right|^2 + \left|\frac{[yj_n(y)]' + B_n[yh_n^{(1)}(y)]'}{y}\right|^2\right) , \tag{8}$$

where j_n and $h_n^{(1)}$ are the spherical Bessel functions, $y = 2\pi(a+d)/\lambda$, and the Mie coefficients A_n and B_n may be found in Ref. 5.

We have performed some numerical comparisons of the results in Eqs. (5) and (6) with those in Eqs. (7) and (8), where we have generally restricted ourselves to cases with $d \ll \lambda$ and $a \ll \lambda$, for which both the IT and dipole approximations should be good. Moreover, these conditions are often realizable in actual situations. However, this still leaves no restriction on the comparison between

d and a. We have performed calculations for a Ag sphere and for the emission frequency set at 3 eV (i.e., $\lambda \sim 4133$ Å).[7] Figure 1 shows the results from the GN model (dashed lines) compared with the exact theory (solid lines) for a = 400 Å, from which we observe already appreciable discrepancies for the GN model with such a realistic size of the sphere. We have also repeated the same calculations for a = 100 Å where the GN model has indeed been found to lie close to the exact theory. Figure 2 shows the comparison at a fixed d = 100 Å with various values of a, where it is clearly shown that the GN model is accurate only when $a/d \lesssim 2.5$ in this situation. The discrepancy arises because of both the dipole and the "single-system" approximation made in the GN model. This latter approximation leads to the fact that the oscillatory behavior of γ^R/γ_0 versus a/d totally disappears in the GN model. It may be of interest to mention that similar oscillating behavior has been observed for the flat-surface case due to the interference between the reflected field at the dipole site with the dipole oscillator itself.[8] Moreover, it has also been acknowledged by GN that their results cannot yield the correct asymptotic results for a flat surface in the limit $a \rightarrow \infty$ with a fixed value of d,[6] whereas it has been noted that Eqs. (7) and (8) can indeed lead back to the correct flat-surface limit.[2] We have further shown that these discrepancies do not arise from the dipole approximation alone. In Fig. 3 we show similar calculations as in Fig. 2 for the range $0 < a/d < 4$ with d fixed at 50 Å, which implies that $a/\lambda \lesssim 0.048$. Discrepancies are obvious in spite of the fact that the dipole approximation should hold for such a small ratio of a/λ. Hence, we conclude that one must be very careful about the limitations of the GN model when it is applied to the dipole-sphere system. In addition to the conditions $a \ll \lambda$ and $d \ll \lambda$ as noted before, the value of a cannot be too large for a fixed d. Since some of the previous calculations do

not exhibit an awareness of this condition,[9] it would be of interest to re-examine all the problems on surface-enhanced Raman scattering and other photochemical processes as previously treated by GN adopting their model for the molecular decay rates.[4]

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6. The details of these results obtained by GN can be found within an appendix to J. Chem. Phys. 1981 75, 1139, which is deposited with the Physics Auxiliary Publication Service and compiled as AIP document No. PAPS JCP SA-75-1139-32.

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8. Chance, R. R.; Prock, A.; Silbey, R. Adv. Chem. Phys. 1978, 37, 1.

9. See, e.g., Fig. 1 of Ref. 4.

Figure Captions

1. Comparison of the GN model for the radiative rates with the exact dynamical theory. The sphere has a fixed radius with $a = 400$ Å, and all other information is given in the text.

2. Same as Fig. 1, except that a is varied and d is fixed at 100 Å. Note that the scale of the y-axis is not uniform.

3. Same as Fig. 2, except that d is fixed at 50 Å.

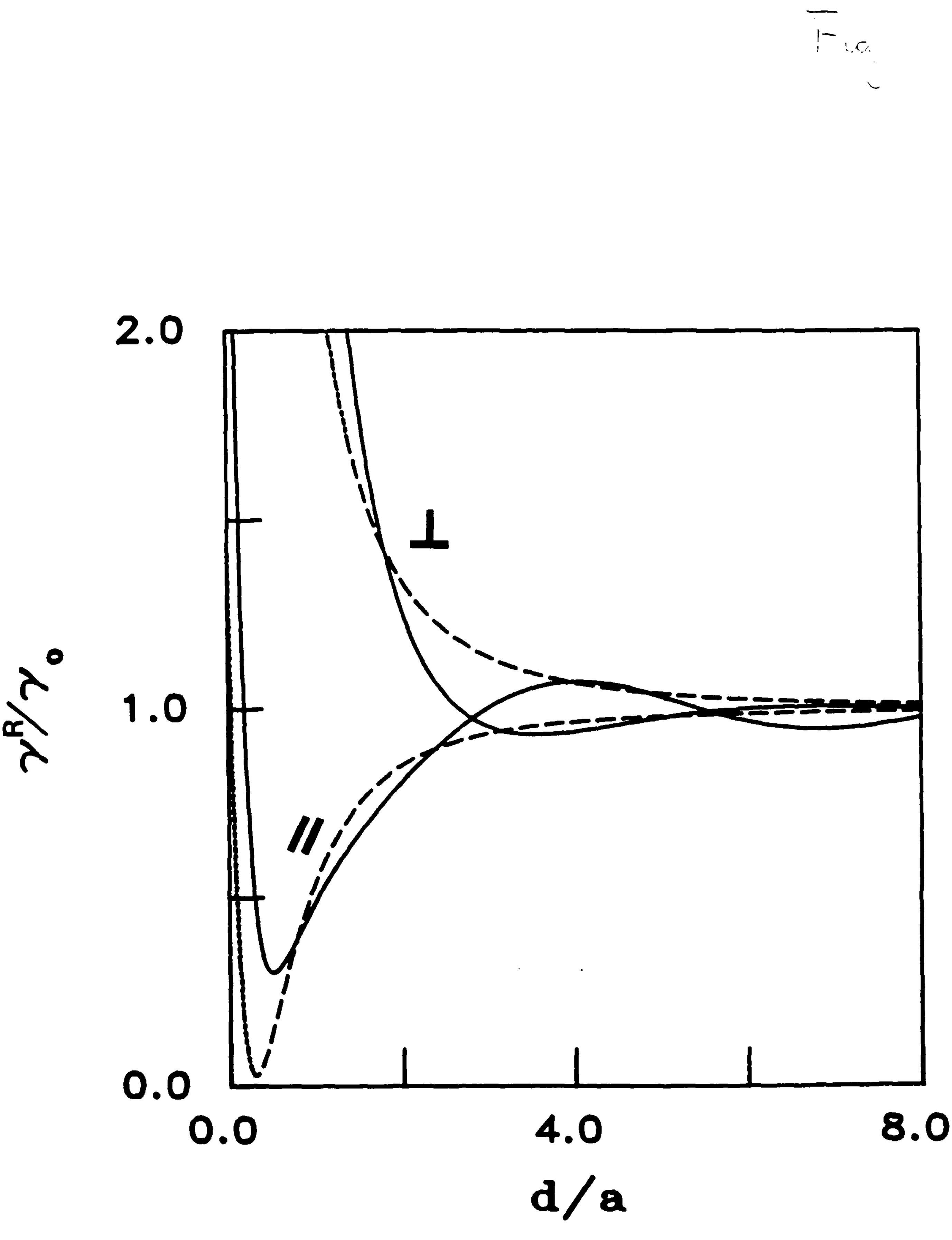

Fig
2.0
1.0
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γ^R/γ_o
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Fig. 2

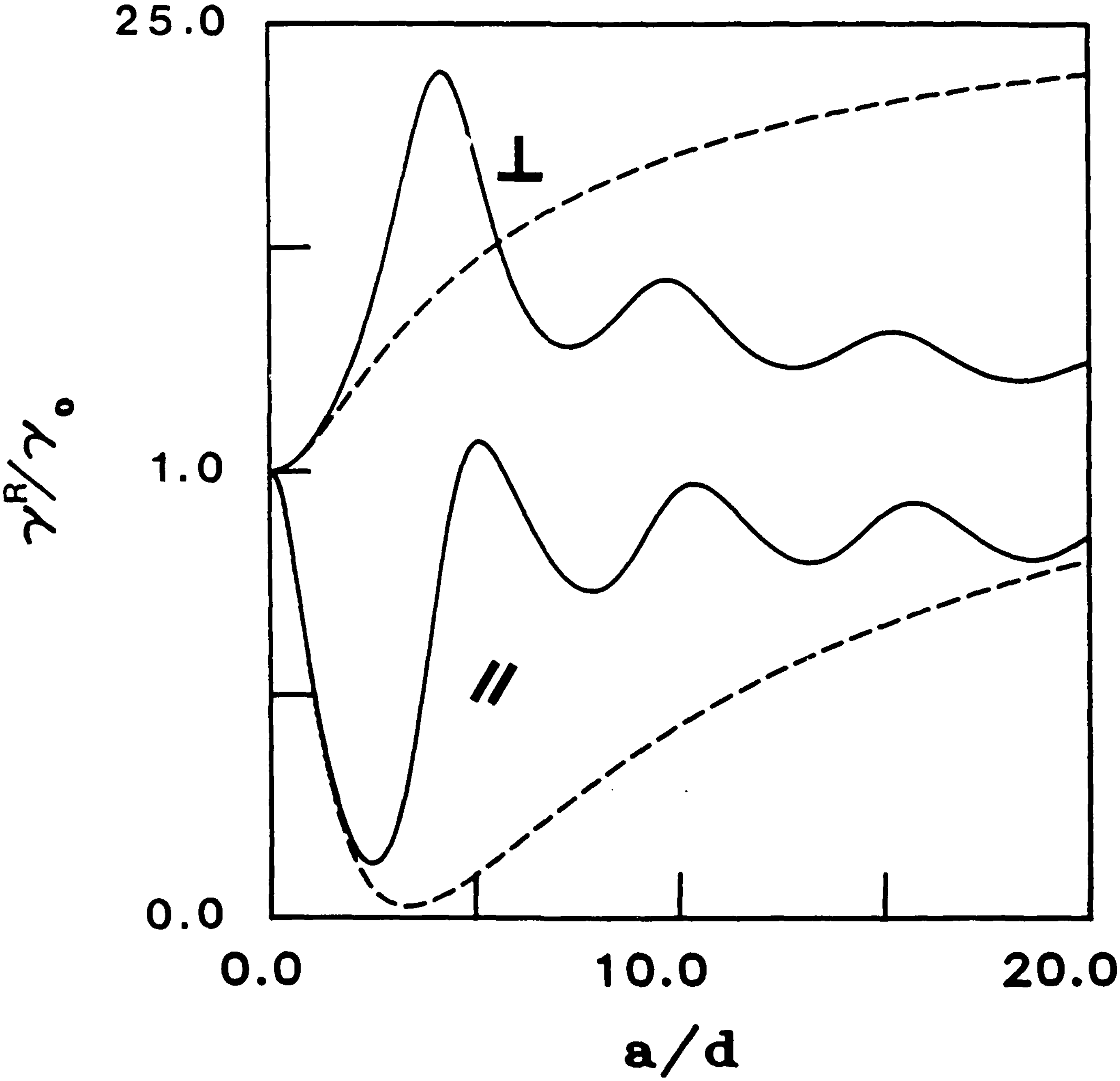
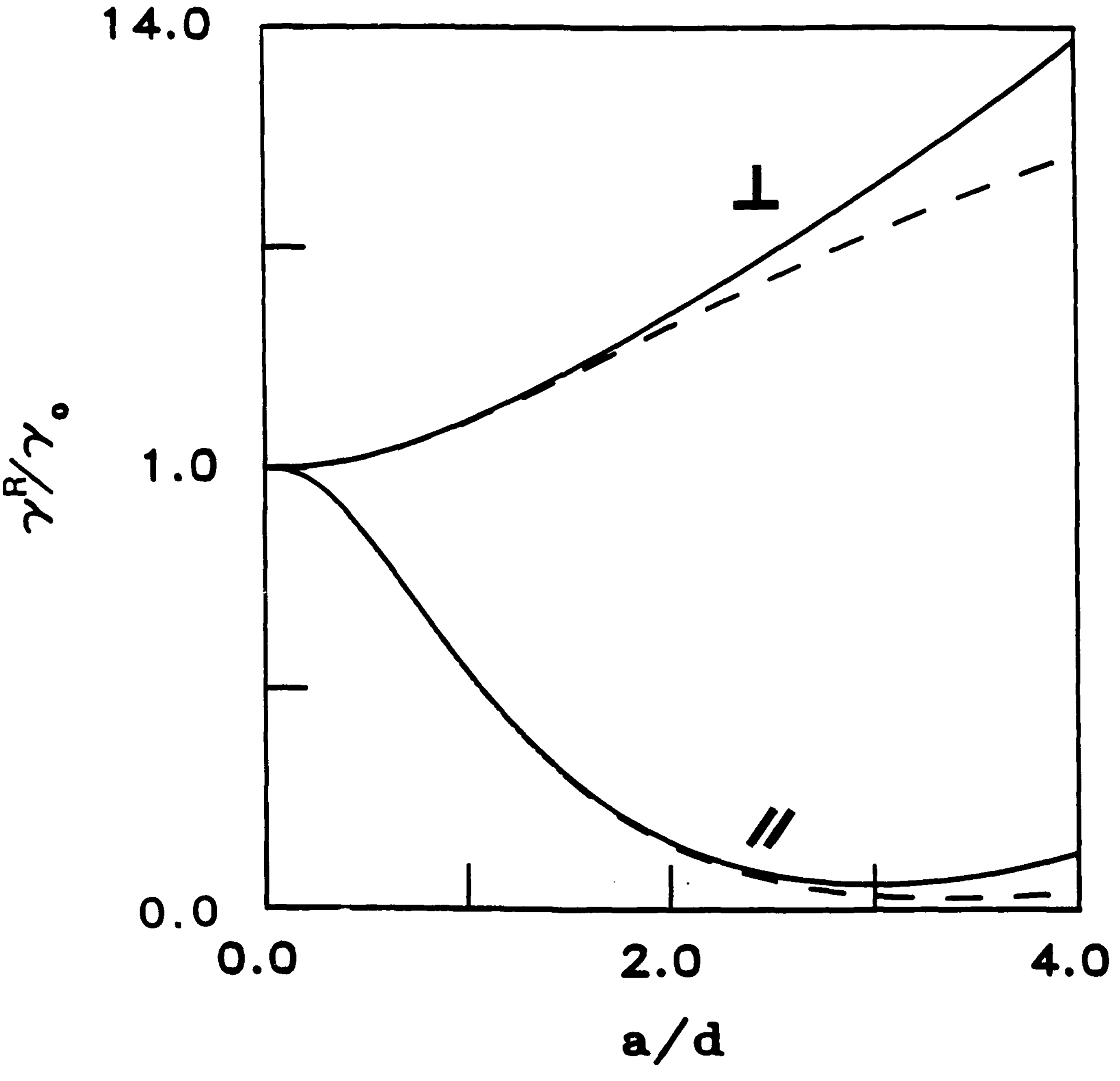


Fig. 3



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